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Diaquabis(ethylenediamine)nickel(II) Bis(*p*-toluenesulfonate) Monohydrate 층상 화합물의 합성과 구조 분석

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Synthesis and Structural Analysis of the Diaquabis(ethylenediamine)nickel(II) Bis(*p*-toluenesulfonate) Monohydrate

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Abstract : The layer structure of the title compound, $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2(\text{H}_2\text{O})$ (en = ethylenediamine), consists of discrete cations, anions, and solvate water molecules linked by a hydrogen bonding network. The central Ni atom of the cation layer has a slightly distorted octahedral coordination geometry with the ethylenediamine ligands functioning as a *N,N'*-bidentate and the water ligands bonding through oxygen in a trans arrangement. The *p*-toluenesulfonate of the anion layer has an alternate sulfonate group directed toward opposite side of the cation layer. This layer structure is stabilized by a hydrogen bond involving the O atoms of the sulfonate, the water ligand, solvate water molecule, and the N atoms of the ethylenediamine.

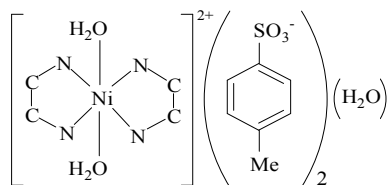
Key words : nickel compound, *p*-toluenesulfonic acid, ethylenediamine, layered material, structure analysis

1. Introduction

Layered inorganic oxoanion compounds have been of great interest, because of their possible use as ion exchangers, adsorbents and catalysts.¹ Particularly synthetic compounds such as metal phosphates and natural minerals such as aluminosilicate clays have been extensively studied.^{2,3} Most commonly, these layered compounds contain covalent metal-oxygen-nonmetal frameworks. In recent years, Squattrito and co-workers

have studied metal organosulfonate compounds as a new family of layered materials, and reported transition metal organosulfonate compounds^{4,5} with layered structures analogous to the recently reported metal phosphonates. In our group, research has been focused to develop new layered and porous materials using organosulfonate and diamine ligands.^{6,7} This approach takes advantage of the flexible coordination behavior of the SO_3^- group and the chelating behavior of the diamine group. In this paper, we report the preparation and crystal structure of the nickel(II) sulfonate complex (I) which was chelated by ethylenediamine ligands.

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Scheme 1. Structural chemical diagram of (I).

2. Experimental

2.1. Preparation and Analysis of



An aqueous solution (15 mL) of *p*-toluenesulfonic acid (1.90 g, 10 mmol) was added to an aqueous solution (15 mL) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2.38 g, 10 mmol). To this mixture solution, neat ethylenediamine (0.74 g, 10 mmol) was dropwise added with stirring. From the resulting solution, a small amount of white precipitates was formed and was filtered off. The filtered solution was allowed to stand in a refrigerator at 5 °C. After a few weeks, the blue block crystals suitable for X-ray analysis were obtained.

IR spectrum of the crystal was recorded with a BioRad Digilab FTS-165 infrared spectrophotometer. Ethylenediamine, *p*-toluenesulfonic acid and water molecule were assigned by the relevant IR absorption bands, respectively.⁸ The contents of the carbon, hydrogen, nitrogen, sulfur and oxygen were analyzed by a CE EA-1110 elemental analyzer. The content of the nickel was analyzed by a Jobin-Yvon Ultima-C inductively coupled plasma-atomic emission spectrometer. The composition of the crystal (I) was deduced from the elemental analyses; the formula of $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2(\text{H}_2\text{O})$ is consistent with the results of X-ray single crystallography. *Anal. Found*: C 37.29, H 6.13, N 9.71, O 24.93, S 11.26, Ni 10.08%. *Calc. for* $\text{C}_{18}\text{H}_{36}\text{N}_4\text{O}_9\text{S}_2\text{Ni}$: C 37.58, H 6.31, N 9.74, O 25.03, S 11.15, Ni 10.20%.

2.2. X-ray Crystallography

A blue block crystal of the title compound was coated with epoxy glue in order to prevent spontaneous liberation of water molecules from the specimen under

ambient conditions. The crystal was mounted on a Siemens P4 four-circle X-ray diffractometer and intensity data were collected in the Θ -2 Θ scan mode using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The cell parameters and orientation matrix were determined from the least-squares fit of 39 reflections in the 2Θ range of 10~25 °. Three standard reflections were measured every 97 reflections: no remarkable decays were observed throughout data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on the psi-scans was applied.⁹

Table 1. Crystallographic and experimental data for (I)

Formula	$\text{C}_{18}\text{H}_{36}\text{N}_4\text{O}_9\text{S}_2\text{Ni}$
Formula weight	575.34
Crystal system	monoclinic
Space group	$P2_1$
<i>a</i> (Å)	10.622(2)
<i>b</i> (Å)	9.148(1)
<i>c</i> (Å)	14.062(2)
β (°)	103.73(1)
<i>V</i> (Å ³)	1327.3(3)
<i>Z</i>	2
<i>D_c</i> , <i>D_m</i> (g/cm ³)	1.440, 1.44(1)
<i>F</i> (000)	608
μ (Mo-K α) (mm ⁻¹)	0.939
2 Θ range for data (°)	4 ~ 53
Limiting indices	$-1 \leq h \leq 13$, $-11 \leq k \leq 1$, $-17 \leq l \leq 17$
Reflections collected	3835
Independent reflections	3301 [$R_{\text{int}} = 0.0217$]
Parameters	332
Goodness-of-fit on <i>F</i> ²	1.044
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0270$, $wR_2 = 0.0689$

All calculations were carried out using the Siemens SHELXTL crystallographic software programs.¹⁰ The space group was assigned based on the systematic absences and intensity statistics, and was confirmed by successful refinements. The structure was solved by the direct method¹¹ and refined by successive full-matrix least-squares method followed by difference Fourier maps. All the non-hydrogen atoms were refined

anisotropically; all the hydrogen atoms fixed at the calculated positions with the isotropic thermal parameters were included in the final structure factor calculations. Final difference of electron density maps contained no significant features. The crystallographic and experimental data are summarized in *Table 1*.

3. Results and Discussion

This compound contains one discrete $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ cation, two *p*-toluenesulfonate anions and one solvate

Table 2. Selected bond lengths (Å) and angles (°) for (I)

Ni(1)-O(1w)	2.131(2)	Ni(1)-O(2w)	2.105(3)
Ni(1)-N(1)	2.087(3)	Ni(1)-N(4)	2.095(3)
Ni(1)-N(5)	2.101(2)	Ni(1)-N(8)	2.097(3)
N(1)-C(2)	1.480(5)	C(2)-C(3)	1.510(5)
C(3)-N(4)	1.470(4)	N(5)-C(6)	1.475(5)
C(6)-C(7)	1.507(5)	C(7)-N(8)	1.476(5)
S(10)-O(11)	1.461(3)	S(10)-O(12)	1.437(4)
S(10)-O(13)	1.438(3)	S(10)-C(11)	1.767(3)
C(11)-C(12)	1.373(4)	C(12)-C(13)	1.376(5)
C(13)-C(14)	1.367(6)	C(14)-C(15)	1.385(6)
C(15)-C(16)	1.381(5)	C(16)-C(11)	1.373(5)
C(14)-C(17)	1.519(6)		
O(1w)-Ni(1)-O(2w)	178.9(1)	O(1w)-Ni(1)-N(1)	89.0(1)
O(1w)-Ni(1)-N(4)	89.6(1)	O(1w)-Ni(1)-N(5)	91.3(1)
O(1w)-Ni(1)-N(8)	92.4(1)	O(2w)-Ni(1)-N(1)	89.0(1)
O(2w)-Ni(1)-N(4)	89.4(1)	O(2w)-Ni(1)-N(5)	89.1(1)
O(2w)-Ni(1)-N(8)	88.6(1)	N(1)-Ni(1)-N(4)	83.2(1)
N(1)-Ni(1)-N(5)	179.6(1)	N(1)-Ni(1)-N(8)	97.5(1)
N(4)-Ni(1)-N(5)	96.5(1)	N(4)-Ni(1)-N(8)	177.9(1)
N(5)-Ni(1)-N(8)	82.8(1)	Ni(1)-N(1)-C(2)	107.8(2)
N(1)-C(2)-C(3)	108.9(3)	C(2)-C(3)-N(4)	108.6(3)
C(3)-N(4)-Ni(1)	107.6(2)	Ni(1)-N(5)-C(6)	107.9(2)
N(5)-C(6)-C(7)	108.3(3)	C(6)-C(7)-N(8)	109.2(3)
C(7)-N(8)-Ni(1)	107.8(2)	O(11)-S(10)-O(12)	110.1(2)
O(11)-S(10)-O(13)	113.1(2)	O(12)-S(10)-O(13)	114.0(3)
O(11)-S(10)-C(11)	105.1(2)	O(12)-S(10)-C(11)	106.8(2)
O(13)-S(10)-C(11)	107.2(2)	S(10)-C(11)-C(12)	120.7(3)
S(10)-C(11)-C(16)	119.9(2)	C(11)-C(12)-C(13)	119.7(4)
C(12)-C(13)-C(14)	121.7(3)	C(13)-C(14)-C(15)	118.4(4)
C(13)-C(14)-C(17)	120.8(4)	C(14)-C(15)-C(16)	120.2(4)
C(15)-C(16)-C(11)	120.5(3)	C(15)-C(14)-C(17)	120.8(4)
C(16)-C(11)-C(12)	119.4(3)		

water molecule per formula unit (*Fig. 1*). The Ni(II)

atom is hexa-coordinated by two ethylenediamine ligands attached at the equatorial position and two water molecules at the axial position. Its environmental geometry has a slightly distorted octahedron. The Ni-N lengths range from 2.087(3) to 2.101(2) Å and the Ni-O lengths range from 2.105(3) to 2.131(2) Å. The N-Ni-N angles of intra-ligand range from 82.8(1) to 83.2(1) ° and the N-Ni-N angles of inter-ligand range from 96.5(1) to 97.5(1) ° and range from 177.9(1) to 179.6(1) °. The N-Ni-O angles are in the range 88.6(1)~92.4(1) ° and the O-Ni-O angle is nearly linear. The bond lengths and angles of sulfonate groups and phenyl rings of the *p*-toluenesulfonate anions has high regularity, respectively (*Table 2*). The geometrical data for this anion are consistent with those of the previously reported results.^{6,7}

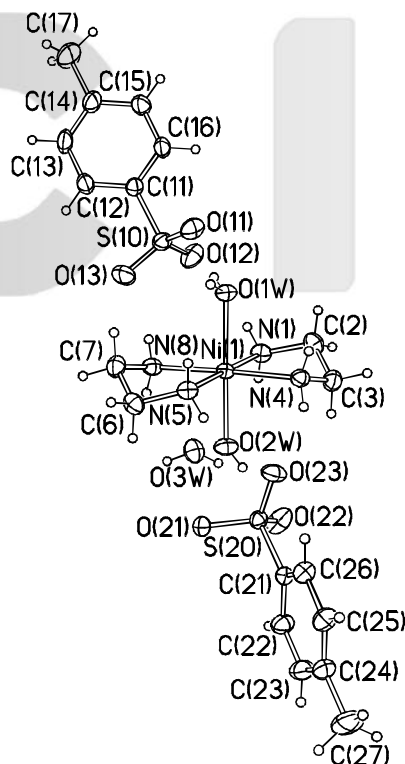


Fig. 1. The molecular structure of (I) with the atomic numbering scheme and displacement ellipsoids at the 30% probability level. Hydrogen atoms are shown as small circles of arbitrary radii.

The extended structure of the title compound (*Fig. 2*)

showed highly layered two-dimensional structure, consists of $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ cation layers and *p*-toluenesulfonate anion layers. There is no direct bonding between the Ni(II) atom and the sulfonate O atoms of the anion.

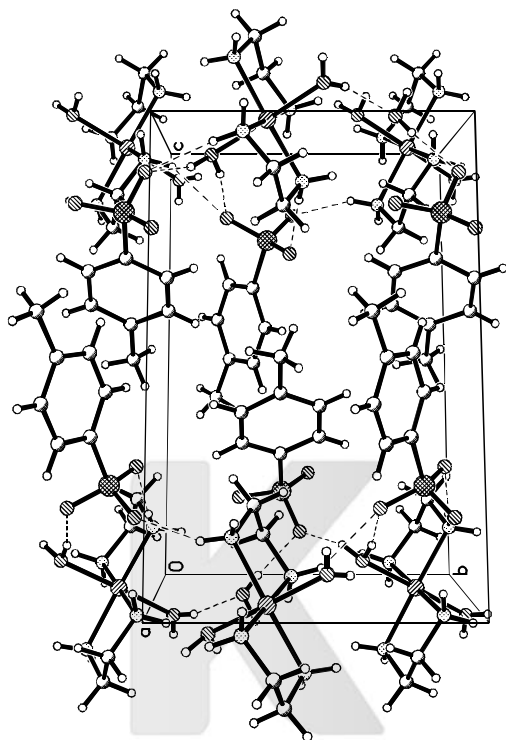


Fig. 2. Perspective view of the unit cell of (I) along the *a* axis; hydrogen bonds are shown by broken lines.

Therefore, the structure of Ni(II) sulfonate compound is quite different from that of the metal phosphonates. The phenyl rings of the *p*-toluenesulfonate anions are approximately perpendicular to the planes of the layers and the sulfonate groups of the *p*-toluenesulfonate anions directed alternately to the opposite sides of the layers. The solvated water molecule is not coordinated to either the sulfonates or the nickel atoms. All the coordinated and uncoordinated water molecules and the O atoms of the *p*-toluenesulfonate anions are linked together in hydrogen bonded chains along [010] with strong $\text{O}_{\text{water}}\text{-H}\cdots\text{O}_{\text{sulfonate}}$ hydrogen bonds { $\text{O}(1\text{w})\text{-H}(1\text{wa})\cdots\text{O}(11)$ 2.67 Å, 163 °; $\text{O}(1\text{w})\text{-H}(1\text{wb})\cdots\text{O}(21)$ 2.73 Å, 161 °; $\text{O}(2\text{w})\text{-H}(2\text{wa})\cdots\text{O}(3\text{w})$ 2.65 Å, 161 °; $\text{O}(2\text{w})\text{-H}(2\text{wb})\cdots\text{O}(22)$ 2.79 Å,

168 °; $\text{O}(3\text{w})\text{-H}(3\text{wa})\cdots\text{O}(11)$ 3.15 Å, 128 °; $\text{O}(3\text{w})\text{-H}(3\text{wa})\cdots\text{O}(12)$ 2.77 Å, 167 °; $\text{O}(3\text{w})\text{-H}(3\text{wb})\cdots\text{O}(21)$ 2.80 Å, 178 °}. These hydrogen bonding chains are crosslinked in the (110) plane by the weak $\text{N}_{\text{diamine}}\text{-H}\cdots\text{O}_{\text{sulfonate}}$ hydrogen bonding { $\text{N}(1)\text{-H}(1\text{a})\cdots\text{O}(11)$ 3.27 Å, 147 °; $\text{N}(4)\text{-H}(4\text{a})\cdots\text{O}(12)$ 3.08 Å, 152 °; $\text{N}(4)\text{-H}(4\text{b})\cdots\text{O}(23)$ 3.38 Å, 153 °; $\text{N}(5)\text{-H}(5\text{b})\cdots\text{O}(21)$ 3.21 Å, 160 °; $\text{N}(5)\text{-H}(5\text{a})\cdots\text{O}(23)$ 3.25 Å, 159 °; $\text{N}(8)\text{-H}(8\text{a})\cdots\text{O}(13)$ 2.99 Å, 166 °; $\text{N}(8)\text{-H}(8\text{b})\cdots\text{O}(23)$ 3.29 Å, 134 °} interactions formed between the amine-H atoms of the ethylenediamine ligands and the sulfonate-O atoms of the *p*-toluenesulfonate anions. Thus, all hydrogen bonds were formed by contacts between cations, anions, and solvate water molecules and extensively contribute to stabilization of the crystal structure.

References

1. S. L. Stuib, *Chem. Rev.*, **93**, 803(1993).
2. G. Alberti, "Comprehensive Supramolecular Chemistry", Vol. 7, 151, J. L. Atwood, J. E. D. Davies, D. D. MacNicol, and F. Vogtle, Eds., Pergamon Press, New York, U.S.A.(1996).
3. A. Clearfield, *Chem. Rev.*, **88**, 125(1988).
4. B. J. Gunderman and P. J. Squattrito, *Inorg. Chem.*, **34**, 2399(1995).
5. A. F. Benedetto, P. J. Squattrito, F. Adani, and E. Montoneri, *Inorg. Chim. Acta*, **260**, 207(1997).
6. C. H. Kim and S. G. Lee, *Anal. Sci. & Tech.* **13**, 534(2000).
7. C. H. Kim and S. G. Lee, *Acta Cryst.* **C57**, 1259(2001).
8. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Part B, John Wiley & Sons, New York, U.S.A.(1997).
9. Siemens, *XSCANS Data Collection Package*, Siemens, Karlsruhe, Germany(1996).
10. Siemens, *SHELXTL Structure Analysis Package*, Siemens, Karlsruhe, Germany(1998).
11. G. M. Sheldrick, *Acta Cryst.*, **A46**, 467(1990).